The Evaluation of High Temperature Adhesive Bonding Processes for Rocket Engine Combustion Chamber Applications

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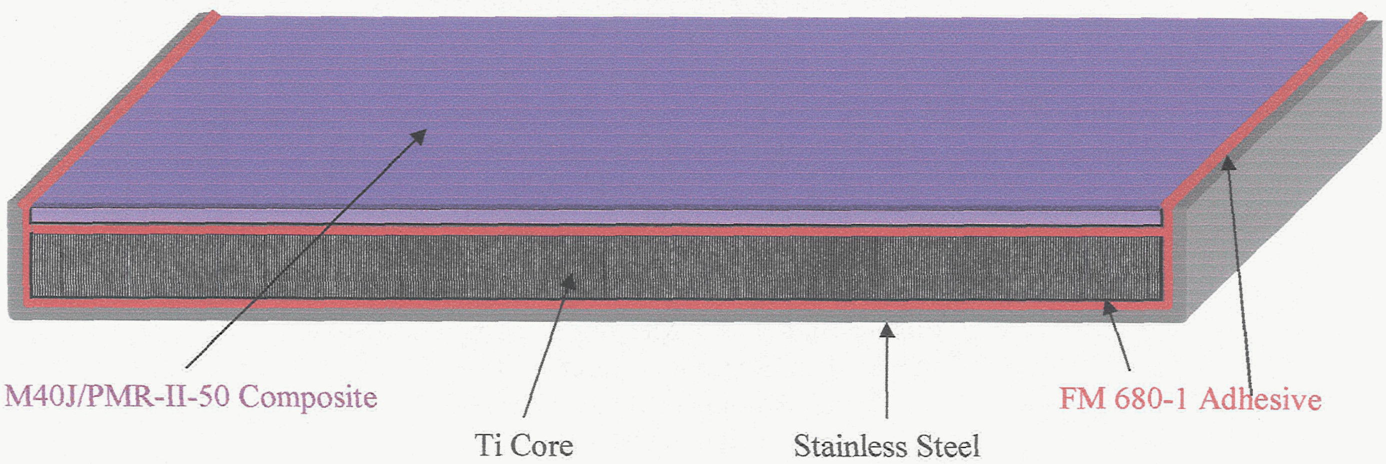
Abstract

NASA Glenn Research Center is currently evaluating the possibility of using high-temperature polymer matrix composites to reinforce the combustion chamber of a rocket engine. One potential design utilizes a honeycomb structure composed of a PMR-II-50/M40J 4HS composite facesheet and titanium honeycomb core to reinforce a stainless steel shell (Figure 1). In order to properly fabricate this structure, adhesive bond processes had to be developed for the titanium core, the stainless steel shell, and the PMR-II-50 composite.

Proper prebond surface preparation is critical in order to obtain an acceptable adhesive bond. Improperly treated surfaces will exhibit decreased bond strength and durability, especially in metallic bonds where interfaces are susceptible to degradation due to heat and moisture. Most treatments for titanium and stainless steel alloys require the use of strong chemicals to etch and clean the surface. These processes are difficult to perform due to limited processing facilities as well as safety and environmental risks and they do not consistently yield optimum bond durability. Boeing Phantom Works previously developed sol-gel surface preparations for titanium alloys using a PETI-5 based polyimide adhesive. In support of part of NASA Glenn Research Center, UDRI and Boeing Phantom Works evaluated variations of this high temperature sol-gel surface preparation, primer type, and primer cure conditions on the adhesion performance of titanium and stainless steel using Cytec FM 680-1 polyimide adhesive. It was also found that a modified cure cycle of the FM 680-1 adhesive, i.e., 4 hrs at 370°F in vacuum + post cure, significantly increased the adhesion strength compared to the manufacturer's suggested cure cycle. In addition, the surface preparation of the PMR-II-50 composite was evaluated in terms of surface cleanness and roughness. This presentation will

discuss the results of strength and durability testing conducted on titanium, stainless steel, and PMR-II-50 composite adherends to evaluate possible bonding processes.

Figure 1: Honeycomb Panel for Rocket Engine Combustion Chamber Wall



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Jacksonville, FL

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Background

- NASA GRC is currently evaluating use of High-Temp PMCs in the design of a rocket engine combustion chamber
- A potential design requires adhesive bonding processes for 3 adherend types:
  - *PMR-II-50 composite*
  - *Stainless steel*
  - *Titanium*

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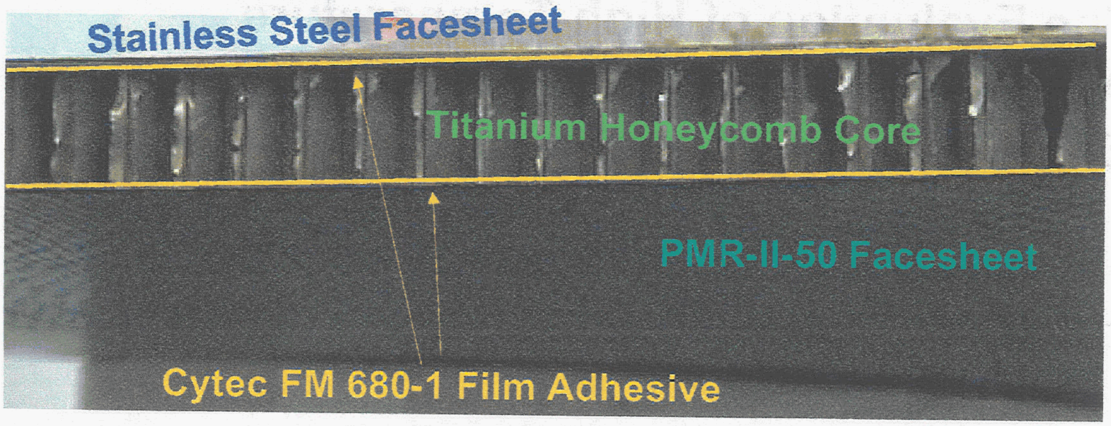
Proposed Bonded Structure



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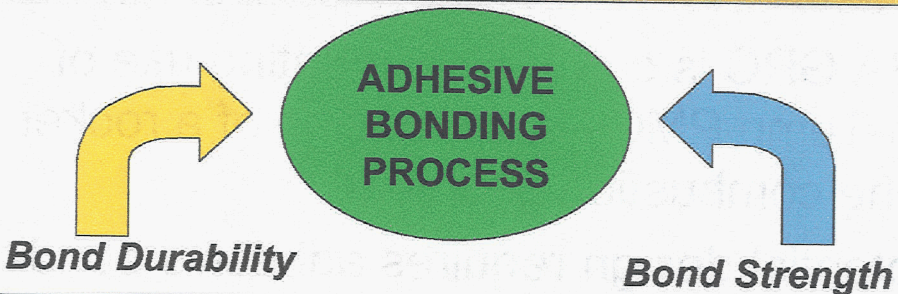
Components of Adhesive Bonding Process



PREBOND SURFACE PREP

Main contributor to environmental durability but can affect strength

- **Titanium core**
- **Stainless Steel facesheet**
- **PMR-II-50 facesheet**

ADHESIVE PROCESSING

Main Contributor to bond strength but can also affect durability

Function of:

- **Cure Temperature**
- **Cure Pressure**
- **Postcure**

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Adhesive Processing

- **Cytec FM 680-1 polyimide adhesive**
  - *0.10 psf, fiberglass woven carrier*
- **Cytec's recommended cure cycle:**
  - ***2 hours at 600°F & 100 psi***
  - ***Postcure for 2-16 hours at 600°F-700°F***
- **Cytec published mechanical data using adherends composed of both Ti-6Al-4V and Avamid N laminates**
  - ***Grit-blast surface preparation***

- Limitations in using recommended cure
  - *Difficult to fabricate a vacuum bag on a complex part with Kapton film*
  - *Large thermal stresses due to CTE mismatch between composite, Ti core, and stainless steel at specified cure temp*

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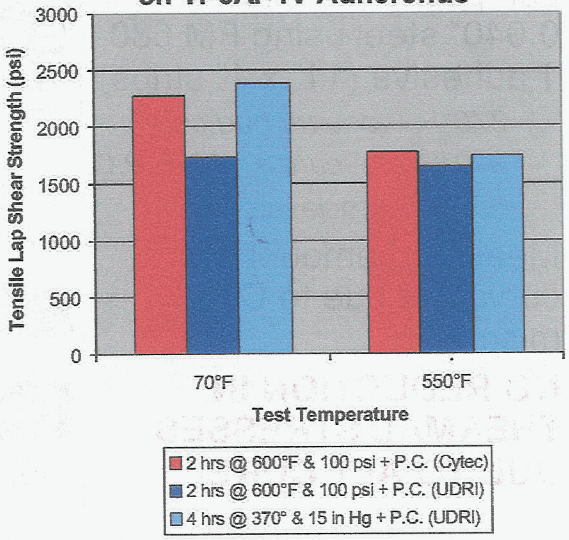
FM 680-1 Adhesive Cure Evaluation

- Proposed alternate cure cycle for FM 680-1:
  - *4 hours at 370°F & 15 in Hg vacuum pressure*
  - *16 hour freestanding postcure at 700°F*
- Allows the use of low temperature bagging films and sealant tapes
  - *Reduces cost*
  - *Easier to process*

Effect of Alternate Cure on FM 680-1 on Ti-6Al-4V Adherends



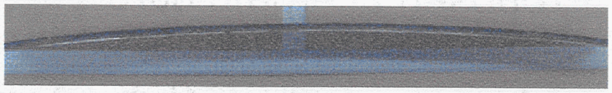
FM 680-1 Alternate Cure Evaluation Summary

- 370°F vacuum cure cycle provided results equivalent to Cytec's published data on grit-blasted Ti-6Al-4V
- Lower temperature cure allows for use of consumable materials with maximum use temperature of 400°F
  - *Lower cost & easier process*
  - *Possible reduction in thermal stresses???*

Residual Stresses Due to CTE Mismatch

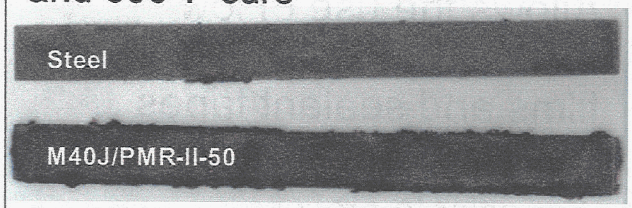
- Bonded M40J/PMR-II-50 composite (12 plies) to 0.040" steel using FM 680-1 adhesive (11" x 1" strips)
  - *370°F, vacuum bag cure*
  - *370°F, v.b. cure + 700°F P.C.*
  - *600°F, autoclave cure*
- Measured amount of curvature due to CTE mismatch
- **NO REDUCTION IN THERMAL STRESSES DUE TO ALT CURE!**

370°F Cure



- **Radius of curvature: ~37 inches**
- **Maximum displacement: 0.36 inches**

370°F Cure with 700°F Postcure and 600°F cure



*** Bond failed in adhesive due to excessive peel stress**

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Prebond Surface Prep
Titanium & Stainless Steel

- Existing surface treatments require the use of strong chemicals and hazardous materials
  - *Difficult to perform*
  - *safety & environmental regulations*
  - *Inconsistent results*
- Boeing Phantom Works developed “Boegel” sol-gel coatings for adhesive bonding to metals
  - *Water-based coating with pH around 8*
  - *Robust process proved under High Speed Civil Transport Program with NASA LaRC using PETI-5*

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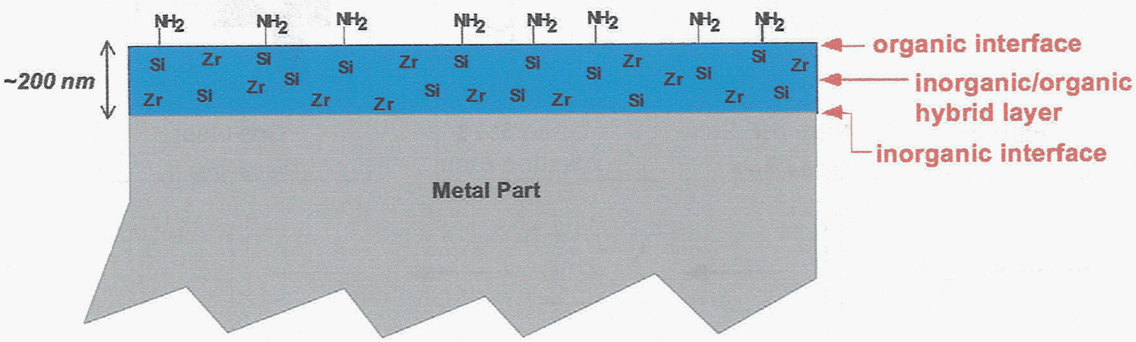
Molecularly Engineered Interfaces

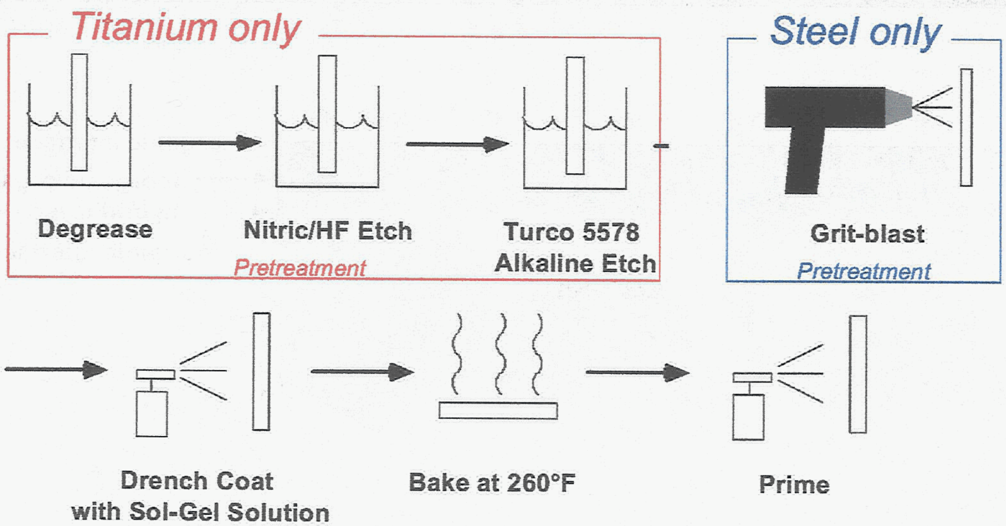


Courtesy of Boeing Phantom Works

Boegel System

- Organic portion of coating tailored to match resin system
  - Aminopropyl and aminophenyl silanes evaluated
- Zirconium an integral part of the coating
  - Ties together functionalized silicon components
  - Improves hydrolytic stability
  - Better match to titanium and stainless steel interface
  - Free energy of Zr alloying into Ti part is higher than Si, Al, or Ti oxides

Sol-Gel Process Overview



Courtesy of Boeing Phantom Works

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Sol-Gel Surface Preparation Evaluation

Processing Variables

- Sol-Gel Chemistry
  - Boegel AM (Aminopropyl)
  - Aminopropyl + Aminophenyl silane (APS + APhS)
  - No sol-gel
- Bond Primer
  - Cytec BR 680
  - No bond primer
- Primer Cure Temps
  - 400°F or 600°F

Materials

- Adherends
  - Ti-6Al-4V
  - Stainless Steel
- Cytec FM 680-1 Adhesive

Test Conditions

- Tensile Lap Shear ASTM D 1002
  - Room Temperature (RT)
  - 600°F dry
  - RT after 3 day water boil exposure

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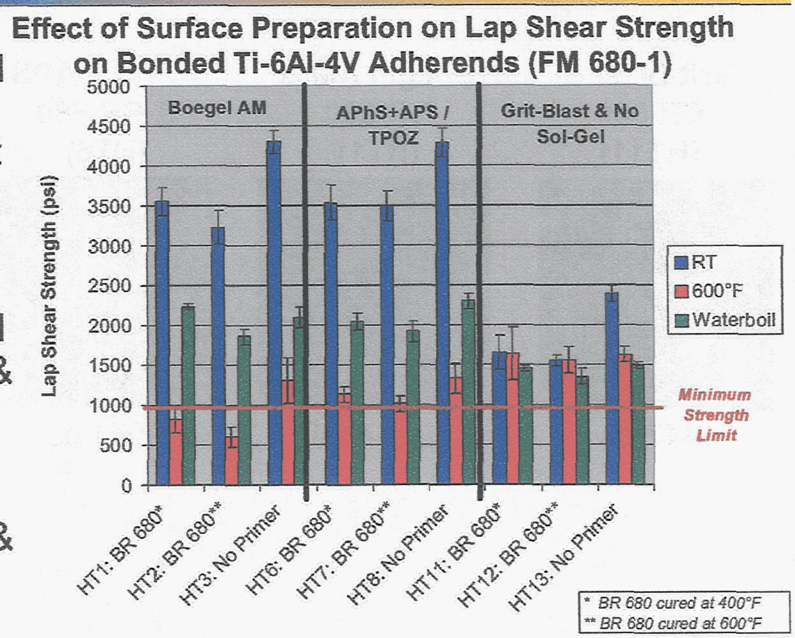
Ti-6Al-4V Lap Shear Results

- Specimens treated with both sol-gel chemistries exhibit higher strength @ RT than grit-blast controls
- APhS+APS sol-gel specimens (HT 6 & 7) exhibit better strength at 600°F than Boegel AM specimens (HT 1 & 2)



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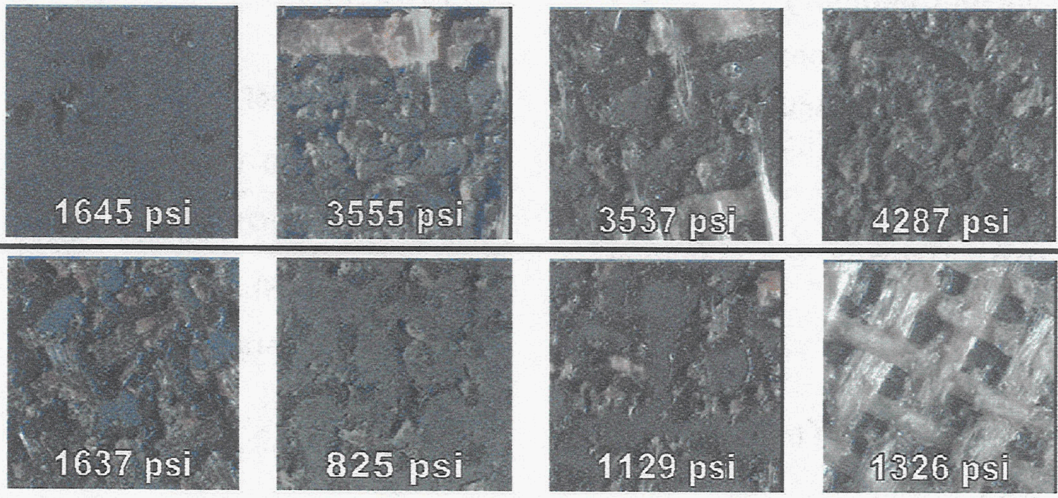
Evaluation of Ti-6-4 Failure Modes (30x)

	Grit-blast & BR 680 (HT11)	Boegel AM & BR 680 (HT1)	APhS + APS & BR 680 (HT6)	APhS + APS no primer (HT8)
RT	1645 psi	3555 psi	3537 psi	4287 psi
600°F	1637 psi	825 psi	1129 psi	1326 psi



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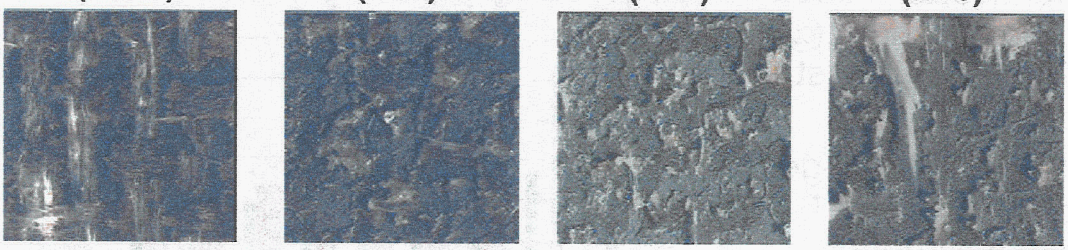
Ti-6-4 Water Boil Failure Modes (30x)

Grit-blast & BR 680 (HT11)	Boegel AM & BR 680 (HT1)	APhS + APS & BR 680 (HT6)	APhS + APS no primer (HT8)
1447 psi	2232 psi	2041 psi	2300 psi



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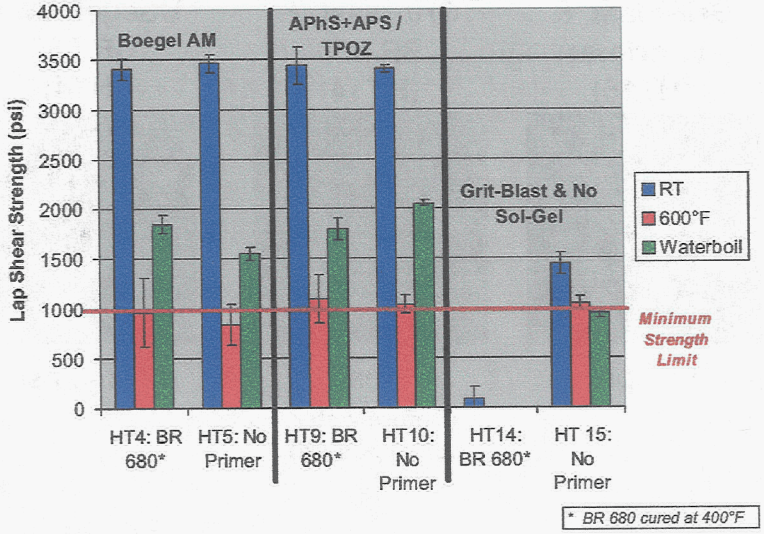
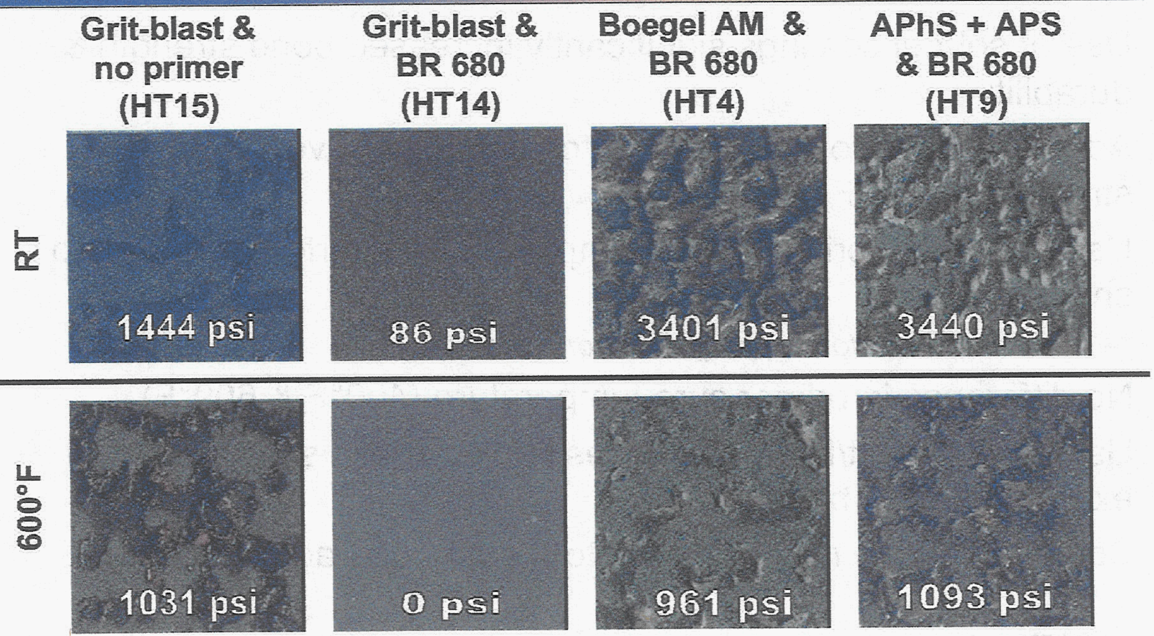
Stainless Steel Lap Shear Results

- Addition of sol-gels improved RT strength
- APhS+APS sol-gel specimens exhibited better failure modes (higher % cohesive) than Boegel AM sol-gel specimens
- Specimens fell apart before testing when BR 680 primer was used without sol-gel (HT14)
  - *Complete interfacial failure*

Effect of Surface Preparation on Lap Shear Strength on Bonded Steel Adherends (FM 680-1)

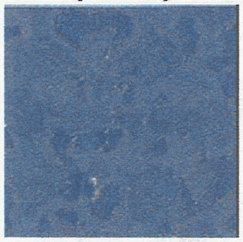


Evaluation of Steel Failure Modes (30x)



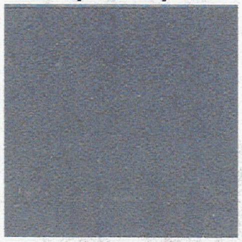
Steel Water Boil Failure Modes (30x)

Grit-blast & no primer (HT15)



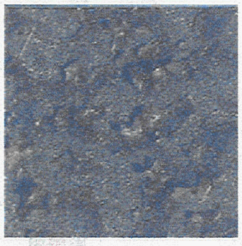
1031 psi

Grit-blast & BR 680 (HT14)



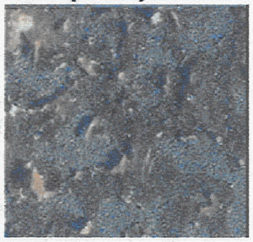
0 psi
(Before water boil exposure)

Boegel AM & BR 680 (HT4)



1845 psi

APhS + APS & BR 680 (HT9)



1798 psi

Sol-Gel Testing Summary

- Use of sol-gel coatings significantly increased bond strength & durability
- Addition of aminophenyl silane to sol-gel improved lap shear strength at 600°F
- Use of BR 680 primer did not improve bond performance in lap shear test
  - *Primer needed for shipping and storing treated parts*
- No difference in primer cure temperature (400°F & 600°F)
- Use of "grit-blast/BR 680" process on stainless steel produced extremely weak bonds
- Sol-gel interface is susceptible to thermal degradation at 600°F

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Prebond Surface Prep
PMR-II-50 Composite

- Main objective is to remove the release ply imprint & contaminates while roughening the surface without exposing or damaging fibers
- Existing surface preparations for PMCs include:
  - *Abrasion with sandpaper*
  - *Grit-blasting*
- Evaluated process was grit-blasting with 50 micron Al_2O_3 grit

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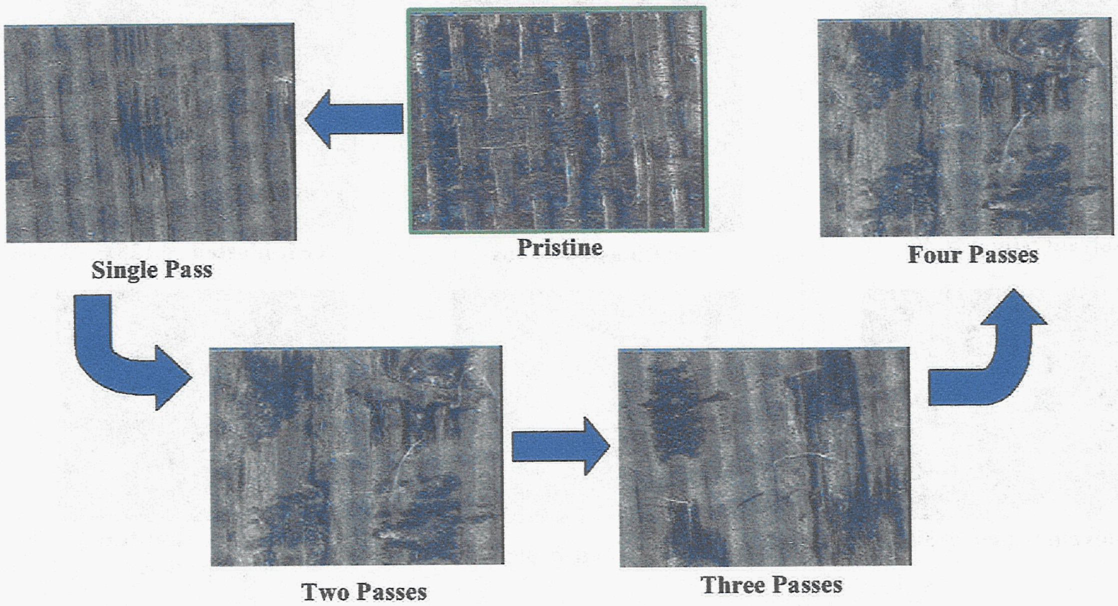
Effect of Grit-Blasting (50µ Al_2O_3 @ 60 psi) on M60J/PMR-II-50 Composite (30X)



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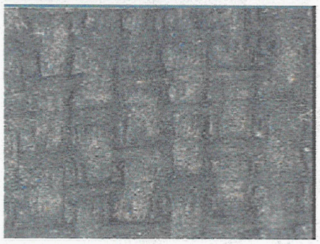
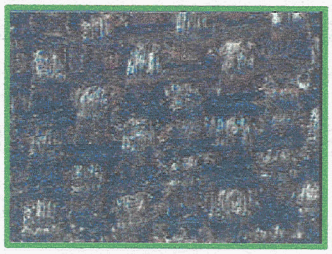
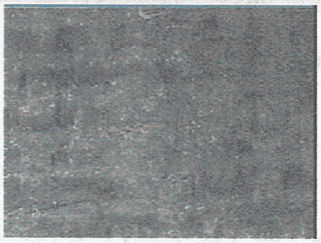
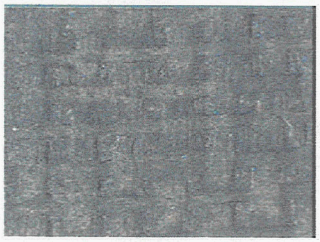
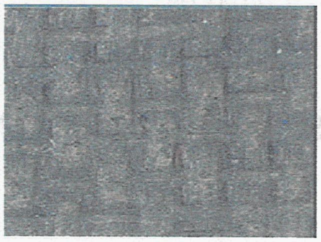
Effect of Grit-Blasting (50µ Al_2O_3 @ 60 psi) on M40J/PMR-II-50 Composite (30X)

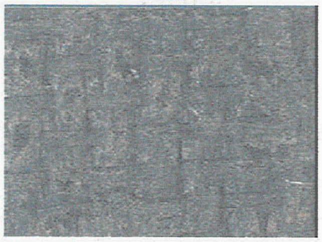

2 Passes


Pristine


10 Passes


4 Passes


6 Passes


8 Passes

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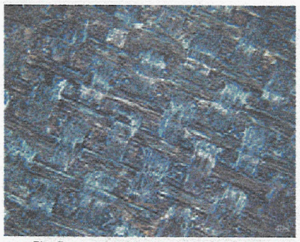
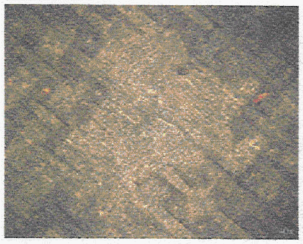
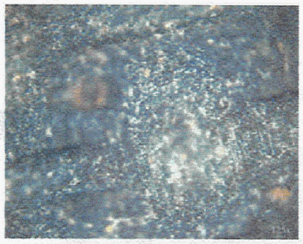
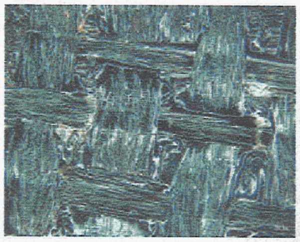
NASA GRC Microscopy M40J/PMR-II-50 Composite

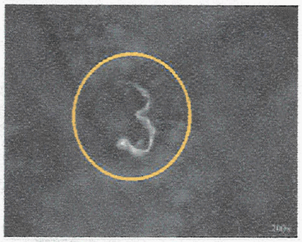

Solvent wiped @ 40x


Grit-blasted @ 40x


Grit-blasted @ 125x


Solvent wiped @ 80x

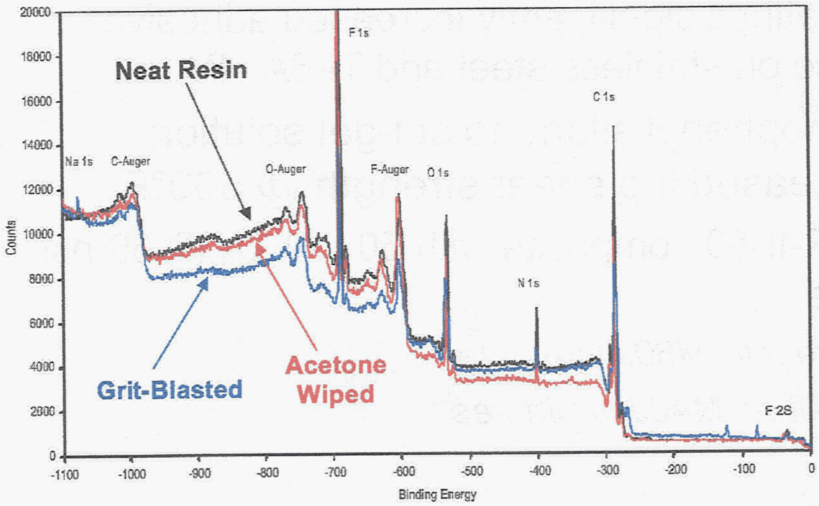

Grit-blasted @ 80x


Remnant of lint-free wipe @ 200x

X-Ray Photoelectron Spectroscopy (XPS)

- Purpose was to verify removal of Teflon-coated peel ply from composite bonding surface
  - *Compared grit-blasted to non-grit-blasted*
- Increase in % Al, Na, & O in grit-blast sample
  - *Due to remnant grit*
- F/C ratio decreased after grit-blasting
  - *Could be due to removal of Teflon or exposing fibers*
- Additional data analysis underway

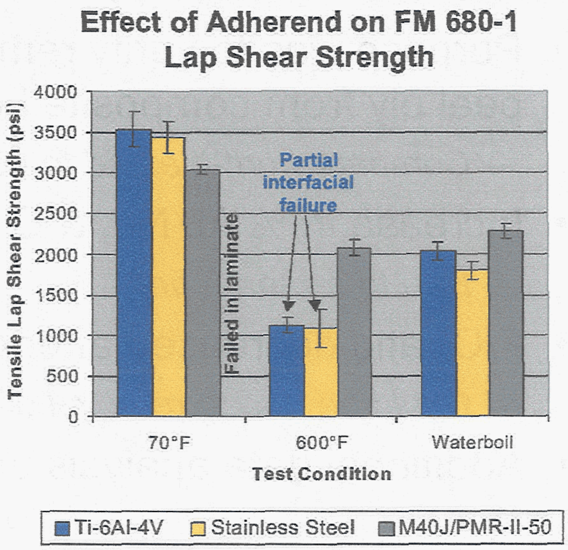
XPS Survey Spectra



Atomic Percent	Neat Resin	Acetone Wiped	Grit-Blasted
C	55.1	57.9	64.2
F	25.1	25.5	13.1
O	12.8	11.8	14.6
N	7.0	4.3	2.9
Si	-	0.5	0.1
Al	-	-	3.5
Na	-	-	1.6
F/C	0.46	0.44	0.20

Lap Shear Strength Using Best Performing Processes

- APhS+APS sol-gel used with Ti & steel specimens
  - *BR 680-1 cured at 400°F*
- Cytec FM 680-1
  - *4 hrs @ 370°F & 15 in Hg*
  - *Postcured for 16 hrs at 700°F*
- PMR-II-50 RT specimens failed in laminate
  - *Bond stronger than composite*



Summary of Results

- Lower temp, nonautoclave cure identified for FM 680-1
- Use of sol-gel coatings significantly increased adhesive bond performance on stainless steel and Ti-6Al-4V
- Addition of Aminophenyl silane to sol-gel solution significantly increased lap shear strength @ 600°F
- Grit-blasting PMR-II-50 composite with 50μ Al_2O_3 @ 60 psi had mixed results
  - *Induced damage into M60J laminates*
  - *Worked very well on M40J laminates*

Future Work

- Fabricate full-scale combustion chamber
- Improve thermal resistance of sol-gel coating
  - *Improve failure modes at 600°F*

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Acknowledgements

- James Mazza & Brett Bolan, AFRL/MLSA
  - *Technical input*
- Ken Combs, UDRI (AFRL/MLSC)
  - *Performing 600°F testing*
- Molly Brown, SOCHE (AFRL/MLSA)
  - *Fabrication of CTE strips and RT testing*

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